

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 22/07, 22/36	A1	(11) International Publication Number: WO 95/25831 (43) International Publication Date: 28 September 1995 (28.09.95)
(21) International Application Number: PCT/US95/03192 (22) International Filing Date: 21 March 1995 (21.03.95) (30) Priority Data: 6/53779 24 March 1994 (24.03.94) JP 6/307639 12 December 1994 (12.12.94) JP (71) Applicant (for all designated States except US): HENKEL CORPORATION [US/US]; Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): IINO, Yasuo [JP/JP]; 1-2-23-305, Goten, Hiratsuka-shi, Kanagawa-ken 254 (JP). SHIMIZU, Akio [JP/JP]; 103 Lumieru Takehi, 625-2, Shimo-Ochiai, Isehara-shi, Kanagawa-ken 259-11 (JP). MO-TOZAWA, Masahiro [JP/JP]; Nihon Parkerizing Hiratsuka Dormitory, 2566, Shinomiya, Hiratsuka-shi, Kanagawa-ken 254 (JP). (74) Agent: DRACH, John, E.; Henkel Corporation, Suite 150, 140 Germantown Pike, Plymouth Meeting, PA 19462 (US).		(81) Designated States: AU, BR, CA, MX, RU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: COMPOSITION AND PROCESS FOR TREATING THE SURFACE OF ALUMINIFEROUS METALS (57) Abstract An aqueous liquid composition that has a pH from 1 to 4.0 and comprises from 1 to 80 pbw (parts by weight) of phosphorus, from 1 to 15 pbw stoichiometric equivalent as zirconium atoms from soluble zirconium compounds, from 3 to 100 pbw stoichiometric equivalent as fluorine atoms of soluble fluorides, and from 1 to 100 pbw of oxidant rapidly produces a very corrosion-resistant and highly paint-adherent coating on the surface of aluminiferous metals when contacted with them at 30 °C to 50 °C for 2 to 30 seconds followed by a water rinse and drying by heating.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LV	Luxembourg	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Larvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

Description

COMPOSITION AND PROCESS FOR TREATING THE SURFACE OF ALUMINIFEROUS METALS

Technical Field

This invention relates to a novel composition and method for treating the surfaces of aluminiferous metals, defined as aluminum and aluminum alloys which contain at least 45 % by weight of aluminum, in order thereby to provide such metal surfaces prior to their painting with an excellent corrosion resistance and paint adherence. This invention may be applied with particularly good effects to the surface treatment of aluminum drawn-and-ironed (hereinafter usually abbreviated "DI") can stock. More specifically, in the case of aluminum DI cans fabricated by the drawing-and-ironing of aluminum alloy sheet, the surface treatment composition and method according to the present invention are able to provide the surface of the can, prior to the painting or printing thereof, with an excellent corrosion resistance and paint adherence in a much shorter period of time than in prior art methods.

Background Art

Baths for treating the surface of aluminiferous metals may be broadly classified into chromate-type treatment baths and non-chromate-type treatment baths. The chromate-type treatment baths typically occur as chromic acid chromate conversion treatment baths and phosphoric acid chromate conversion treatment baths. Chromic acid chromate conversion treatment baths were first utilized in about 1950 and are in wide use even at present, for example, for heat exchanger-fins and the like. Chromic acid chromate conversion treatment baths contain chromic acid (CrO_3) and hydrofluoric acid (HF) as their base components, and may contain a conversion accelerator as desired. These baths form a conversion coating on the metal surface that contains small amounts of hexavalent chromium.

The phosphoric acid chromate conversion treatment bath was invented in 1945 (United States Patent Number 2,438,877). This conversion bath contains chromic acid (CrO_3), phosphoric acid (H_3PO_4), and hydrofluoric acid (HF) as its base components. The main component in the coating produced by this

bath is hydrated chromium phosphate ($\text{CrPO}_4 \cdot 4\text{H}_2\text{O}$). Since this conversion coating does not contain hexavalent chromium, this bath is also in wide use at present as, for example, a paint undercoat treatment for the lid and body of beverage cans.

5 The above-described chromate-type surface treatment baths contain toxic hexavalent chromium, but environmental considerations make it desirable to use hexavalent chromium-free treatment baths. The treatment bath taught in Japanese Patent Application Laid Open [Kokai or Unexamined] Number Sho 52-131937 [131,937/1977] is typical of inventions relating to non-chromate-type
10 (chromium-free) surface treatment baths. This treatment bath is an acidic (pH = approximately 1.0 to 4.0) waterborne coating solution that contains phosphate, fluoride, and zirconium or titanium or both. Treatment of metal surfaces with this non-chromate-type surface treatment bath produces thereon a conversion film whose main component is zirconium or titanium oxide.

15 Non-chromate-type treatment baths are currently widely used for aluminum DI cans because they offer the advantage of being free of hexavalent chromium, although treatment times of at least 15 seconds are required with these baths in order to obtain an industrially satisfactory performance (corrosion resistance). On the other hand, shortening the surface treatment time in the surface
20 treatment of aluminiferous metals has become an important issue. This is due to the desire — created by recent increases in aluminum DI can production levels — to substantially raise the aluminum DI can manufacturing speed and the desire to reduce the size of surface treatment facilities in order to conserve space.

25 The surfaces of aluminum DI cans at present are treated mainly with phosphoric acid chromate treatment baths and zirconium-containing non-chromate treatment baths. The outside bottom surface of a DI can body is generally not painted during the aluminum DI can manufacturing process, but is subjected to high-temperature sterilization. If its corrosion resistance is poor, the aluminum will become oxidized at this point and a blackening discoloration will occur. This
30 phenomenon is generally known as "blackening". It is for this reason that the (unpainted) coating produced by surface treatment must itself exhibit a high corrosion resistance.

The treatment method taught in Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 1-246370 [246,370/1989] is one example of an invention directed at shortening the surface treatment time under consideration. In this method, the surface of the aluminiferous metal is first cleaned with an alkaline degreaser and the cleaned surface is thereafter treated with an acidic solution (pH = 1.5 to 4.0) containing 0.01 to 0.5 g/L of zirconium ions, 0.01 to 0.5 g/L of phosphate ions, and 0.001 to 0.05 g/L of effective F ions, and optionally 0.01 to 1 g/L of vanadium ions. This method, however, does not afford an industrially satisfactory blackening resistance.

A non-chromate treatment method is disclosed in Japanese Patent Publication Number Sho 57-39314 [39,314/1982]. In this method, the surface of aluminiferous metal is treated with an acidic solution containing titanium salt and/or zirconium salt, hydrogen peroxide, and phosphoric acid and/or condensed phosphoric acid. This treatment bath is, however, unstable, and it also exhibits an unsatisfactory reactivity in terms of surface film formation. Nor does this disclosure specifically describe the treatment temperature, treatment time, or treatment process. Finally, it is difficult to obtain an industrially stable blackening resistance using the method disclosed in Japanese Patent Publication Number Sho 57-39314.

Disclosure of the Invention

Problems to Be Solved by the Invention

The present invention seeks to solve the problems described above for the prior art. In specific terms, the present invention introduces a stable composition for treating the surface of aluminiferous metals that is able to rapidly impart an excellent corrosion resistance and paint adherence to the surface of aluminiferous metals. This invention also introduces a surface treatment method that uses said composition.

Summary of the Invention and Description of Preferred Embodiments

The present inventors discovered that a very corrosion-resistant and highly paint-adherent coating could be rapidly formed on the surface of aluminiferous metal by execution of a surface treatment method comprising (a) contacting the aluminiferous metal surface, preferably at 30° C to 50° C, with an aqueous

surface treatment composition, also called a "bath" for brevity even though it can be used for spraying as well as immersion, said bath comprising, preferably consisting essentially of, or more preferably consisting of, water and a mixture in specific proportions of phosphate ions, zirconium compound, fluoride, and oxidant, (b) then rinsing the treatment bath-bearing surface of the metal with water, and (c) drying by heating. The present invention was achieved based on this discovery.

The bath according to the present invention for treating the surface of aluminiferous metals characteristically comprises 1 to 80 parts by weight (hereinafter usually abbreviated "pbw") of phosphate ions, zirconium compound at 1 to 15 pbw as zirconium atoms, fluoride at 3 to 100 pbw as fluorine atoms, and 1 to 100 pbw of oxidant.

The method according to the present invention for treating the surface of aluminiferous metals characteristically comprises contacting the surface of aluminiferous metal for 2 to 30 seconds at 30° C to 50° C with a surface treatment bath containing the above-described surface treatment composition, then rinsing the treated metal surface with water, and thereafter drying by heating.

The surface treatment composition according to the present invention is an acidic aqueous treatment bath whose essential ingredient is a mixture of phosphate ions, zirconium compound, fluoride, and oxidant. Of particular importance is the joint use of fluoride and oxidant in the surface treatment composition according to the present invention and the surface treatment bath used by the surface treatment method according to the present invention. This joint use of fluoride and oxidant has the surprising effects of stabilizing the surface treatment bath and inducing a substantial improvement in both the corrosion resistance (resistance to blackening) and paint adherence of the resulting surface coating.

The surface treatment composition according to the present invention is an aqueous bath of a mixture that contains the following components in the following weight proportions:

phosphate ions	1	-	80	pbw
zirconium compound (as zirconium atoms)	1	-	15	pbw
fluoride (as fluorine atoms)	3	-	100	pbw

oxidant 1 - 100 pbw

Its general pH range is 1.0 to 4.0.

Execution of the method according to the present invention requires the preparation of a surface treatment bath (aqueous solution) containing the above-described surface treatment composition. This preparation is preferably carried out so as to give the following concentrations for the various components in the subject surface treatment bath.

phosphate ions	0.01	-	0.8	g/L
zirconium compound (as zirconium atoms)	0.01	-	0.15	g/L
fluoride (as fluorine atoms)	0.03	-	1	g/L
oxidant	0.01	-	1	g/L

The pH of this surface treatment bath is preferably adjusted into the range from 2.0 to 4.0.

Phosphoric acid (H_3PO_4), its salts, and the like can be used to introduce phosphate ions into the surface treatment composition according to the present invention. The phosphate ions content in the above-described component recipe for the surface treatment composition according to the present invention ranges from 1 to 80 pbw, while the preferred range is from 3 to 20 pbw. The corresponding surface treatment bath is poorly reactive and good film formation does not usually occur when the phosphate ions content in the above-described component recipe falls below 1 pbw. While a good-quality film can be formed at above 80 pbw, the effect from the phosphate ions is saturated at such levels, which are therefore uneconomical since they serve only to raise the cost of the treatment bath.

The source of the zirconium compound in the surface treatment composition according to the present invention is not critical, and the oxides, hydroxides, nitrates, fluorides, and the like of zirconium can be used as the zirconium compound source. The zirconium compound content in the above-described component recipe for the surface treatment composition according to the present invention ranges from 1 to 15 pbw as zirconium atoms, while the preferred zirconium compound content ranges from 4 to 8 pbw as zirconium atoms. The corresponding surface treatment bath will not form a good-quality film when the zir-

conium content falls below 1 weight part. The quality of the film no longer improves at amounts in excess of 15 pbw and such levels are therefore uneconomical since they serve only to raise the cost of the treatment bath.

5 The fluoride source for the surface treatment composition according to the present invention is not critical, and acids such as hydrofluoric acid (HF), fluozirconic acid (H_2ZrF_6), fluotitanic acid (H_2TiF_6), fluosilicic acid, fluoboric acid, and the like, and the salts of these acids may be used as the fluoride source. The fluoride content in the above-described component recipe for the surface treatment composition according to the present invention ranges from 3 to 100 pbw
10 as fluorine atoms. The preferred fluoride content ranges from 3 to 60 pbw as fluorine atoms. The corresponding surface treatment bath is poorly reactive and good film formation does not occur when the fluoride content falls below 3 pbw. The use of amounts in excess of 100 pbw is undesirable because the corresponding increase in metal etching causes a degraded appearance. The treatment bath requires the presence of the fluoride in order to stabilize — as aluminum fluoride — the aluminum that elutes into the treatment bath. As a result, the
15 optimal fluoride content in the surface treatment bath used by the method of the present invention will vary as a function of the concentration of aluminum eluting from the metal workpiece. For example, the fluorine concentration must be approximately 0.2 g/L when the aluminum concentration in the surface treatment
20 bath is 0.1 g/L.

The type of oxidant in the surface treatment composition according to the present invention is not critical. Useable oxidants include hydrogen peroxide; acids such as nitrous acid, tungstic acid, molybdic acid, peroxy acids such as
25 peroxophosphoric acid, etc.; salts of the preceding acids; and the like. Hydrogen peroxide is the most preferred oxidant based on the ease of waste water treatment after use of a surface treatment bath containing subject composition. The function of the oxidant in the surface treatment composition and treatment method according to the present invention is to accelerate the reaction rate for zirconium film formation on the metal surface. The oxidant content in the above-described component recipe for the surface treatment composition according to the
30 present invention ranges from 1 to 100 pbw. The preferred oxidant content rang-

es from 20 to 50 pbw. When the oxidant content is less than 1 pbw, the above-described reaction accelerating activity will not be observed when surface treatment is carried out using the corresponding surface treatment bath. Although no technical problems are associated with levels in excess of 100 pbw, the effect of this component is saturated at such levels and they are therefore uneconomical, because they serve only to raise the cost of the treatment bath.

The general range for the pH of the surface treatment composition according to the present invention is 1.0 to 4.0. The surface treatment bath used by the method according to the present invention preferably has a pH of 2.0 to 4.0. pH values below 2.0 often cause an excessive etch of the metal surface and can impede formation of the conversion film. Values in excess of 4.0 will in some cases impede the formation of a highly corrosion-resistant film. The range of 2.3 to 3.0 is an even more preferred pH range for the surface treatment bath used in the method according to the present invention. The pH of the surface treatment bath can be adjusted in the method according to the present invention through the use of acids, such as phosphoric acid, nitric acid, hydrochloric acid, hydrofluoric acid, etc., or through the use of alkali, such as sodium hydroxide, sodium carbonate, ammonium hydroxide, etc.

When the metal treated by the method according to the present invention is an alloy of aluminum with, for example, copper, manganese, etc., the stability of the treatment bath can be substantially impaired by elution into the surface treatment bath of metal ions deriving from the copper, manganese, etc., component of the aluminum alloy. In cases such as this, an organic acid, such as gluconic acid, oxalic acid, etc., may be added to the surface treatment bath in order to chelate this metal alloying component.

The details of the surface treatment method according to the present invention will now be explained. The method according to the present invention uses a surface treatment bath according to the present invention. When the surface treatment bath takes the form of a concentrate, it is diluted with water to the desired concentration prior to use in the method according to the present invention.

Preferred expanded surface treatment process steps:

- (1) Surface cleaning: degreasing — an acidic, alkaline, or solvent-based degreaser may be used
- (2) water rinse
- 5 (3) characteristic surface treatment (application of a surface treatment bath according to the present invention)
treatment temperature: 30° C to 50° C
treatment method: immersion or spraying
treatment time: 2 to 30 seconds
- 10 (4) water rinse
- (5) rinse with de-ionized water
- (6) drying

Contact between the metal and surface treatment bath preferably is carried out at 35° C to 50° C in the surface treatment method according to the present invention. Contact temperatures below 35° C sometimes result in inadequate reaction between the metal surface and treatment bath, which prevents the formation of a good-quality film. The zirconium compound in the treatment bath may become unstable at temperatures above 50° C, with the undesirable result that a portion of the zirconium compound will precipitate.

20 The method according to the present invention can be executed by immersing the metal in the surface treatment bath, in which case the immersion treatment time preferably should be 2 to 30 seconds. Immersion times below 2 seconds usually result in inadequate reaction between the treatment bath and metal surface, which prevents the formation of a film with good corrosion resistance. Immersion times in excess of 30 seconds do not normally yield any additional improvements in the properties of the resulting conversion coatings. Thus, preferred immersion treatment times range from 2 to 30 seconds, while immersion times ranging from 5 to 15 seconds are more particularly preferred.

30 Contact may also be executed in the method according to the present invention by spraying the treatment bath onto the metal surface. The occurrence of a pH increase in the vicinity of the interface with the metal surface may become problematic when spray treatment is carried out by continuously spraying

the treatment bath, and in some cases a satisfactory film formation will not occur. It is for this reason that use of an intermittent spray is preferred. Said intermittent spraying preferably consists of at least two sprays separated by an interval of 1 to 5 seconds. The surface treatment bath/metal surface contact time (sum of the spray and non-spray time intervals) in this case should again range from 2 to 30 seconds. Contact times below 2 seconds often result in an inadequate reaction and prevent the formation of a film with good corrosion resistance. No additional improvement in performance is normally obtained for contact times in excess of 30 seconds. Spraying at least twice with separation by an interval of 2 to 3 seconds is a particularly preferred technique, and the preferred overall contact time is 5 to 10 seconds.

The add-on of the surface coating formed on aluminiferous metal by the invention method is preferably 7 to 18 mg/m² as zirconium. An inadequate corrosion resistance by the resulting surface coating may result when the surface coating weight is less than 7 mg/m² as zirconium. The paint adherence of the resulting surface coating will in some cases be unsatisfactory when the surface coating weight exceeds 18 mg/m² as zirconium.

The aluminiferous metals whose surface may be treated by the invention method encompass aluminum and aluminum alloys, wherein the aluminum alloys are exemplified by Al-Mn alloys, Al-Mg alloys, Al-Si alloys, and the like.

The aluminiferous metal that may be subjected to the invention method is not specifically restricted with respect to shape or dimensions, and, for example, sheet, various types of moldings, and the like may be subjected to the method according to the present invention.

The surface treatment composition and surface treatment method according to the present invention are further illustrated by the following working examples, and the benefits of the invention may be further appreciated by comparison to the comparison examples.

Examples

(1) Specimens

Aluminum DI can (fabricated by the DI processing of aluminum sheet) was cleaned with a hot aqueous solution of an acidic degreaser (PALKLIN™ 500,

registered trademark of Nihon Parkerizing Company, Limited) and then subjected to surface treatment.

(2) Evaluation Methods

(a) Corrosion resistance

5 The corrosion resistance of the aluminum DI can was evaluated based on the resistance to blackening by boiling water. The boiling water blackening resistance was determined by immersing the surface-treated aluminum DI can in boiling tap water for 30 minutes and then visually evaluating the extent of discoloration (blackening) thereby produced. The results of this test are reported on
10 the following scale:

+	:	no blackening
x	:	partial blackening
x x	:	blackening over entire surface

(b) Paint adherence

15 The surface of the surface-treated aluminum can was coated to a paint film thickness of 5 to 7 micrometers with an epoxy-urea can paint. This was followed by baking for 4 minutes at 215° C. A 5 mm x 150 mm strip was then cut from the painted can, and polyamide film was hot-press bonded at 200° C to the painted surface of the strip to give a test specimen. The test specimen thus prepared was subjected to a 180° peel test in which the peel strength was measured
20 during peeling of the polyamide film from the test specimen. Higher peel strength values in this test are indicative of a better paint adherence by the surface-treated aluminum can, and peel strength values equal to or greater than 4.0 kilograms-force per 5 millimeters of width (hereinafter usually abbreviated "kgf/
25 5mm") are generally regarded as satisfactory for practical applications.

Example 1

 A cleaned aluminum DI can as described above was sprayed with surface treatment bath 1 (with a composition given below) heated to 40° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 3 second intervals (for a total of 12 seconds). The treated surface was then rinsed with tap
30 water and thereafter sprayed for 10 seconds with de-ionized water (with a resistivity of at least 3,000,000 ohm-cm). The aluminum DI can was subsequently

dried in a hot-air drying oven at 180° C for 2 minutes and submitted to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 1 ("ppm" hereinafter means parts per million by weight)

5	75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions: 50 ppm)
	20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
	20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
	30 % hydrogen peroxide (H_2O_2)	322 ppm	(H_2O_2 : 100 ppm)

pH: 3.0 (adjusted with aqueous ammonia)

Example 2

10 A cleaned aluminum DI can was immersed for 15 seconds in surface treatment bath 2 (with a composition given below) heated to 50° C. The DI can was removed from the surface treatment bath and then rinsed with water, rinsed with deionized water, and dried according to the procedure in Example 1. The
15 resulting DI can was submitted to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 2

	75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions: 50 ppm)
	20 % fluozirconic acid (H_2ZrF_6)	1000 ppm	(Zr: 88 ppm)
20	20 % hydrofluoric acid (HF)	210 ppm	(F: 150 ppm)
	30 % hydrogen peroxide (H_2O_2)	166 ppm	(H_2O_2 : 50 ppm)

pH: 3.3 (adjusted with aqueous ammonia)

Example 3

25 A cleaned aluminum DI can was sprayed with surface treatment bath 3 (with a composition given below) heated to 50° C. This spray treatment consisted of 2 sprays (2 seconds each) separated by a 1 second interval (total of 5 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was sub-
30 jected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 3

	75 % phosphoric acid (H_3PO_4)	14 ppm	(PO_4 ions: 10 ppm)
	20 % fluozirconic acid (H_2ZrF_6)	1000 ppm	(Zr: 88 ppm)

20 % hydrofluoric acid (HF)	210 ppm	(F: 150 ppm)
30 % hydrogen peroxide (H ₂ O ₂)	1660 ppm	(H ₂ O ₂ : 500 ppm)
pH: 2.5 (adjusted with sodium hydroxide)		

Example 4

6 A cleaned aluminum DI can was sprayed with surface treatment bath 4 (with a composition given below) heated to 50° C. This spray treatment consisted of 6 sprays (3 seconds each) separated by 2 second intervals (total of 28 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was submitted to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 4

75 % phosphoric acid (H ₃ PO ₄)	138 ppm	(PO ₄ ions: 100 ppm)
20 % fluozirconic acid (H ₂ ZrF ₆)	250 ppm	(Zr: 22 ppm)
15 20 % hydrofluoric acid (HF)	100 ppm	(F: 47 ppm)
30 % hydrogen peroxide (H ₂ O ₂)	830 ppm	(H ₂ O ₂ : 250 ppm)
pH: 4.0 (adjusted with aqueous ammonia)		

Example 5

20 A cleaned aluminum DI can was sprayed with surface treatment bath 5 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 5

75 % phosphoric acid (H ₃ PO ₄)	138 ppm	(PO ₄ ions: 100 ppm)
20 % fluozirconic acid (H ₂ ZrF ₆)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
30 30 % hydrogen peroxide (H ₂ O ₂)	322 ppm	(H ₂ O ₂ : 100 ppm)
pH: 2.0 (adjusted with aqueous ammonia)		

Example 6

A cleaned aluminum DI can was sprayed with surface treatment bath 6 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (3 seconds each) separated by 5 second intervals (total of 19 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 6

75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions: 50 ppm)
20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
sodium tungstate ($Na_2WO_4 \cdot 2H_2O$)	1000 ppm	(WO_4 : 800 ppm)
pH: 2.5 (adjusted with nitric acid)		

Example 7

A cleaned aluminum DI can was sprayed with surface treatment bath 7 (with a composition given below) heated to 35° C. This spray treatment consisted of 4 sprays (2 seconds each) separated by 2 second intervals (total of 14 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 7

75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions 50 ppm)
20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
20 % sodium nitrite ($NaNO_2$)	1000 ppm	(NO_2 : 133 ppm)
pH: 2.5 (adjusted with nitric acid)		

Example 8

A cleaned aluminum DI can was sprayed with surface treatment bath 8 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 8

75 % phosphoric acid (H_3PO_4)	690 ppm	(PO_4 ions: 500 ppm)
20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
30 % hydrogen peroxide (H_2O_2)	166 ppm	(H_2O_2 : 50 ppm)
pH: 3.0 (adjusted with nitric acid)		

Example 9

A cleaned aluminum DI can was sprayed with surface treatment bath 9 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 9

75 % phosphoric acid (H_3PO_4)	25 ppm	(PO_4 ions: 18 ppm)
20% fluozirconic acid (H_2ZrF_6)	228 ppm	(Zr: 20 ppm)
20 % hydrofluoric acid (HF)	150 ppm	(F: 54 ppm)
30 % hydrogen peroxide (H_2O_2)	667 ppm	(H_2O_2 : 200 ppm)
pH: 2.5 (adjusted with aqueous ammonia)		

Example 10

A cleaned aluminum DI can was sprayed with surface treatment bath 10 (with a composition given below) heated to 35° C. This spray treatment consisted of 7 sprays (2 seconds each) separated by 2 second intervals (total of 30 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 10

75 % phosphoric acid (H_3PO_4)	14 ppm	(PO_4 ions: 10 ppm)
20 % fluozirconic acid (H_2ZrF_6)	114 ppm	(Zr: 10 ppm)
20 % hydrofluoric acid (HF)	150 ppm	(F: 41 ppm)
30 % hydrogen peroxide (H_2O_2)	3333 ppm	(H_2O_2 : 1000 ppm)

pH: 2.8 (adjusted with aqueous ammonia)

Example 11

A cleaned aluminum DI can was sprayed with surface treatment bath 11 (with a composition given below) heated to 35° C. This spray treatment consisted of a 3-second spray (total of 3 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 11

75 % phosphoric acid (H_3PO_4)	413 ppm	(PO_4 : 300 ppm)
20 % fluozirconic acid (H_2ZrF_6)	1706 ppm	(Zr: 150 ppm)
20 % hydrofluoric acid (HF)	150 ppm	(F: 216 ppm)
30 % hydrogen peroxide (H_2O_2)	16667 ppm	(H_2O_2 : 5000 ppm)

pH: 2.5 (adjusted with aqueous ammonia)

Comparative Example 1

A cleaned aluminum DI can was sprayed with surface treatment bath 12 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 12

75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions: 50 ppm)
20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)

pH: 3.0 (adjusted with aqueous ammonia)

Comparative Example 2

A cleaned aluminum DI can was sprayed with surface treatment bath 13 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was sub-

jected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 13

75 % phosphoric acid (H_3PO_4)	69 ppm	(PO_4 ions: 50 ppm)
20 % fluozirconic acid (H_2ZrF_6)	57 ppm	(Zr: 5 ppm)
5 20 % hydrofluoric acid (HF)	210 ppm	(F: 40 ppm)
pH: 3.0 (adjusted with aqueous ammonia)		

Comparative Example 3

A cleaned aluminum DI can was sprayed with surface treatment bath 14 (with a composition given below) heated to 35° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

Composition of surface treatment bath 14

15 20 % fluozirconic acid (H_2ZrF_6)	500 ppm	(Zr: 44 ppm)
20 % hydrofluoric acid (HF)	210 ppm	(F: 95 ppm)
pH: 3.0 (adjusted with aqueous ammonia)		

Comparative Example 4

A cleaned aluminum DI can was sprayed with a commercial aluminum DI can surface treatment bath (ALODINE™ 404, registered trademark of Nihon Parkerizing Company, Limited) heated to 30° C. This spray treatment consisted of 3 sprays (2 seconds each) separated by 2 second intervals (total of 10 seconds). This was followed by rinsing with water, rinsing with deionized water, and drying according to the procedure in Example 1. The resulting DI can was subjected to evaluation of the corrosion resistance and paint adherence.

The results of the evaluations for the cans treated in Examples 1 - 11 and Comparison Examples 1 - 4 are all reported in Table 1.

As demonstrated by the results in Table 1, an excellent corrosion resistance and an excellent paint adherence were exhibited by the surface coatings produced in Examples 1 to 11, which employed surface treatment baths and surface treatment methods according to the present invention. Comparative surface

treatment baths were used in Comparative Examples 1 to 4, and the surface coatings produced by these comparative baths exhibited a poor corrosion resistance and sometimes a poor paint adherence.

Benefits of the Invention

5 As the preceding discussion has made clear, the surface treatment bath and surface treatment method according to the present invention are able to rapidly produce highly corrosion-resistant and very paint-adherent coatings on the surface of aluminiferous metals prior to the painting thereof. When applied to aluminum DI cans, the surface treatment bath according to the present invention
10 rapidly produces a very corrosion-resistant and paint-adherent coating on the surface of aluminum DI cans prior to its painting or printing. This makes it possible to speed up the manufacturing line and reduce the size requirements (space economization) of the treatment installation.

15 As a result of these features, both the bath and method according to the present invention for treating the surface of aluminiferous metals have a very high practical utility.

Table 1.

5	Example or Comparison Example No.	Resistance to Blackening in Boiling Water	Peel Strength, kgf/5mm	Zr Add-on mg/m ²
	Example 1	+	4.0	10.5
10	Example 2	+	4.0	13.5
	Example 3	+	4.0	7.5
15	Example 4	+	4.0	15.5
	Example 5	+	4.0	12.2
	Example 6	+	4.0	13.5
20	Example 7	+	4.0	11.0
	Example 8	+	4.0	9.8
25	Example 9	+	4.0	8.2
	Example 10	+	4.0	9.7
	Example 11	+	4.0	8.5
30	Comparative Example 1	x	2.5	8.0
35	Comparative Example 2	x x	4.0	3.0
	Comparative Example 3	x x	4.0	6.5
40	Comparative Example 4	x x	2.0	6.0

Claims

1. An aqueous liquid composition for treating the surface of aluminiferous metals, said composition comprising water and:
 - (A) from 1 to 80 pbw of phosphate ions;
 - 5 (B) one or more zirconium compounds in a total amount to correspond stoichiometrically to from 1 to 15 pbw of zirconium atoms;
 - (C) one or more fluorides in a total amount corresponding stoichiometrically to from 3 to 100 pbw of fluorine atoms; and
 - (D) from 1 to 100 pbw of oxidant.
- 10 2. An aqueous liquid composition according to claim 1, wherein the oxidant is hydrogen peroxide.
3. An aqueous liquid composition according to claim 1 or 2, comprising:
 - (A) from 3 to 200 pbw of phosphate ions;
 - (B) one or more zirconium compounds in a total amount to correspond stoichiometrically to from 4 to 8 pbw of zirconium atoms;
 - 15 (C) one or more fluorides in a total amount corresponding stoichiometrically to from 3 to 60 pbw of fluorine atoms; and
 - (D) from 20 to 50 pbw of oxidant.
4. A method for treating an aluminiferous metal surface, said method comprising the steps of:
 - 20 (I) contacting the aluminiferous metal with an aqueous liquid composition according to claim 3 at a temperature in the range from 30 to 50 ° C for a time of 2 to 30 seconds;
 - (II) rinsing the surface contacted in step (I) with water; and
 - 25 (III) drying the surface rinsed in step (II) by heating.
5. A method according to claim 4, wherein the aqueous liquid composition has a pH from 2 to 4.0 and comprises from 0.01 to 0.8 g/L of phosphate ions, from 0.01 to 0.15 g/L stoichiometric equivalent as zirconium atoms, from 0.03 to 1 g/L stoichiometric equivalent as fluorine atoms, and from 0.01 to 1 g/L of
30 oxidant.
6. A method according to claim 4 or 5, wherein the aluminiferous metal

surface is contacted with the aqueous liquid composition by immersing the metal surface in the in the aqueous liquid composition for a time from 2 to 30 seconds.

7. A method according to claim 4 or 5, wherein the aluminiferous metal surface is contacted with the aqueous liquid composition by spraying the metal surface at least once with the aqueous liquid composition, and the total combined time of spraying and of any intervals between the first and the last spraying is from 2 to 30 seconds.

8. A method according to claim 7, wherein the aluminiferous metal surface is sprayed with the aqueous liquid composition at least twice, and there is an interval of 2 to 3 seconds between each period of spraying and the successive period of spraying if any.

9. A method for treating an aluminiferous metal surface, said method comprising the steps of:

- (I) contacting the aluminiferous metal with an aqueous liquid composition according to claim 1 or 2 at a temperature in the range from 30 to 50 ° C for a time of 2 to 30 seconds;
- (II) rinsing the surface contacted in step (I) with water; and
- (III) drying the surface rinsed in step (II) by heating.

10. A method according to claim 9, wherein the aqueous liquid composition has a pH from 2 to 4.0 and comprises from 0.01 to 0.8 g/L of phosphate ions, from 0.01 to 0.15 g/L stoichiometric equivalent as zirconium atoms, from 0.03 to 1 g/L stoichiometric equivalent as fluorine atoms, and from 0.01 to 1 g/L of oxidant.

11. A method according to claim 10, wherein the aluminiferous metal surface is contacted with the aqueous liquid composition by immersing the metal surface in the aqueous liquid composition for a time from 2 to 30 seconds.

12. A method according to claim 10, wherein the aluminiferous metal surface is contacted with the aqueous liquid composition by spraying the metal surface at least once with the aqueous liquid composition, and the total combined time of spraying and of any intervals between the first and the last spraying is from 2 to 30 seconds.

13. A method according to claim 12, wherein the aluminiferous metal surface is sprayed with the aqueous liquid composition at least twice, and there is an interval of 2 to 3 seconds between each period of spraying and the successive period of spraying if any.

5 14. A method according to claim 9, wherein the aluminiferous metal surface is contacted with the aqueous liquid composition by immersing the metal surface in the aqueous liquid composition for a time from 2 to 30 seconds.

15. A method according to claim 9, wherein the aluminiferous metal surface is contacted with the aqueous liquid composition by spraying the metal surface at least once with the aqueous liquid composition, and the total combined time of spraying and of any intervals between the first and the last spraying is from 2 to 30 seconds.

10 16. A method according to claim 15, wherein the aluminiferous metal surface is sprayed with the aqueous liquid composition at least twice, and there is an interval of 2 to 3 seconds between each period of spraying and the successive period of spraying if any.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/03192

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 22/07, 22/36

US CL : 148/247, 253

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/247, 253

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 4,338,140 (REGHI) 06 JULY 1982, col. 3, line 44 - col. 5, line 55.	1 and 3-16 ----- 1 and 3-16
X ---- Y	US, A, 4,422,886 (DAS et al) 27 DECEMBER 1983, col. 3, line 35 - col. 5, line 60 and the examples.	1 and 3-16 ----- 1 and 3-16
X ---- Y	US, A, 4,470,853 (DAS et al) 11 SEPTEMBER 1984, see the examples and the claims.	1 and 3-16 ----- 1 and 3-16
X ---- Y	US, A, 5,139,586 (DAS) 18 AUGUST 1992, col. 5, line 5 - col. 7, line 5.	1 and 3-16 ----- 1 and 3-16

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A		document defining the general state of the art which is not considered to be of particular relevance
* E		earlier document published on or after the international filing date
* L		document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
* O		document referring to an oral disclosure, use, exhibition or other means
* P		document published prior to the international filing date but later than the priority date claimed
	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	* &	document member of the same patent family

Date of the actual completion of the international search

24 APRIL 1995

Date of mailing of the international search report

01 JUN 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ANTHONY GREEN

Telephone No. (703) 308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/03192

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---, P Y	US, A, 5,380,374 (TOMLINSON) 10 JANUARY 1995, see the examples.	1 and 3-16 ----- 1 and 3-16
X --- Y	GB, A, 2,259,920 (GIBSON CHEMICALS LIMITED) 31 MARCH 1993, page 4, line 1 - page 5, line 25.	1 and 3-16 ----- 1 and 3-16
A	DE, A, 3,236,247 (METALLGESELLSCHAFT AG) 12 APRIL 1984, see the abstract.	1-16